Water Quality:

I. Introduction

II. Water Quality

A. **Interactions of fish with their environment**

B. **Need for testing**

C. **Definitions**

D. **Desired Characteristics**

E. **Measurable Parameters**

III. Water Chemistry

A. **Dissolved Oxygen**

B. **Water Temperature**

C. **Carbon Dioxide**

D. **Alkalinity**

E. **Hardness**

F. **Ammonia**

G. **Nitrite**

IV. Testing and Monitoring

Water Quality

A. Interaction of fish with their environment

1. Physical

a. *Temperature*
b. *Dissolved Gases*
c. *Total Solid Load*
d. *Light*

2. Chemical

a. *Water Chemistry*
Parameters of concern:
(1) Ammonia (NH_3)
(2) Nitrite (NO_2)
(3) Nitrate (NO_3)
(4) Carbon Dioxide (CO_2)
(5) Hardness/Alkalinity (as $CaCO_3$)
(6) pH
(7) DO
(8) Trace metals (Cu, Zn, Al, Se, Mn)

b. *Pollution effects*

3. Biological

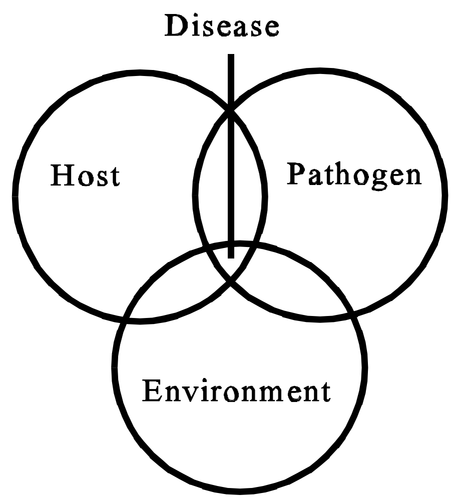
a. *Fish Density*
b. *Other Organisms (bacteria, algae, rooted aquatics, etc)*

4. Procedural (Cultural)

a. *Water Flow*
b. *Feeding Rate and Frequency*
c. *Pond Care (Cultural practices)*
d. *Disease*

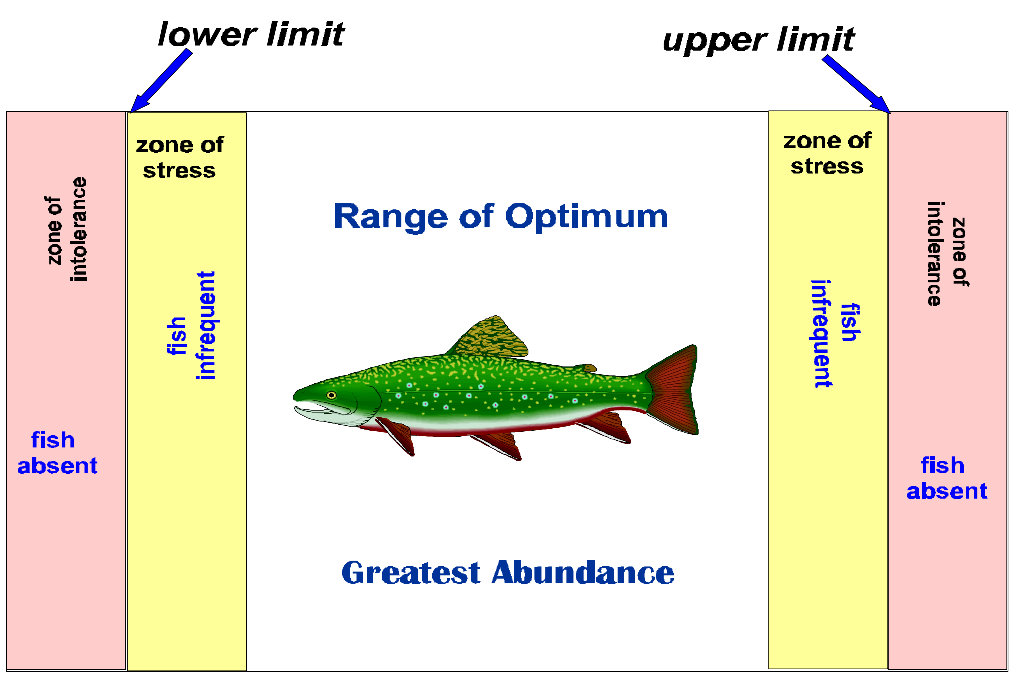
B. Need for Testing

It is important to understand what the physiological limits of the species being raised are. These limits need to be set as boundaries within which you must maintain water quality and other parameters. If we accept Dr. Sniezko's diagramatic representation of fish health and quality (below), then fish hatchery management becomes management of the physiology of the fish.



Only where the three come together is disease produced: ***a susceptable host in a poor environment with a virulent pathogen***

So it it the job of the hatchery manager and fish culturist to see that tolerance limits of the fish are not exceeded. Fish can and do survive in marginal habitats and environments, but if additional challenges are given to them, the chance for mortality is much greater than in optimum environments.



C. Definitions

1. O_2 / DO - dissolved oxygen content of water

2. pH - hydrogen ion concentration; a measure of the buffer capacity of the water

3. Hardness - concentration of salts in water that help prevent large sifts in pH (Buffering)

4. Alkalinity - Quantity and kinds of compounds that collectively shift the pH toward alkaline

5. CO_2 - Carbon dioxide; by-product of respiration

6. Cl^- - Chloride ion concentration

7. NH_4^+ - Ammonium ion concentration; by-product of fish metabolism

8. NH_3 - Ammonia concentration; ammount dependent on pH and temperature

9. NO_2^{2-} - Nitrite concentration; by-product of ammonia oxidation

10. N_2 - Nitrogen gas supersaturation

11. H_2S - Hydrogen sulfide; produced by bacteria

D. Desired Characteristics (for Intensive culture facilities)

1. Groundwater source (i.e. Spring)
2. moderate rainfall
3. moderate gradient to allow gravity flow
4. adequate limestone deposits
5. uniform and moderate temperatures
6. good cover
7. freedom from grazing, logging, mining, agriculture
8. submerged intake
9. covered pipeline
10. moderate gradient from intake area
11. adequate aeration
12. enclosed and covered water supply to prevent surface contamination
13. room for expansion

E. Measurable Parameters

1. Optimum maximum concentrations (Piper *et al* 1982)

Parameter		***Concentration***
DO (dissolved oxygen)		5ppm or greater
CO_2		0-10ppm
Alkalinity (as $CaCO_3$)		10-400ppm
pH		6.5 - 8.0
Hardness (as $CaCO_3$)		10-400ppm
Ca^{2+} (calcium)		4-160ppm
Mg^{2+} (magnesium)		trace
Mn (manganese)		0-0.01ppm
Fe (iron) Total		0-0.15ppm
Fe^{2+} (ferrous)		0
Fe^{3+} (ferric)		0-0.5ppm
P (phosphorous)		0.01-3.0ppm
NO_3 (nitrate)		0-3.3ppm
Zn (zinc)		0-0.05ppm
H_2S (hydrogen sulfide)		0
NH_3 (ammonia- unionized) upper limit		0.0125ppm
N_2 (nitrogen gas) upper limit		110%
Total solids		80ppm

WATER CHEMISTRY

1. Dissolved Oxygen (D.O.)

Temperature and Elevation affect the solubility of Oxygen (O_2) in water. As temperature increases, solubility of O_2 decreases. Likewise, as elevation increases, O_2 solubility decreases. Temperature regulates the carrying capacity of water for O_2. Elevation relates to the effect of atmospheric pressure that forces O_2 into solution.

Dissolved oxygen in ppm for fresh water in equilibrium with air (Leitritz and Lewis 1976).

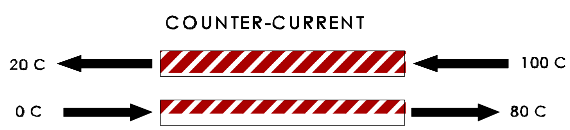
Temp	Elevation in Feet									
(°F)	0	1000	2000	3000	4000	5000	6000	7000	8000	9000
40	13.0	12.5	12.1	11.6	11.2	10.8	10.4	10.0	9.6	9.3
45	12.1	11.7	11.2	10.8	10.5	10.1	9.7	9.3	9.0	8.7
50	11.3	10.9	10.5	10.1	9.8	9.4	9.1	8.7	8.4	8.1
55	10.6	10.3	9.9	9.5	9.2	8.9	8.5	8.2	7.9	7.6
60	10.0	9.6	9.3	8.9	8.6	8.3	8.0	7.7	7.4	7.1
65	9.4	9.1	8.8	8.4	8.1	7.8	7.5	7.2	7.0	6.7
70	9.0	8.7	8.4	8.0	7.8	7.4	7.2	6.9	6.7	6.4
75	8.6	8.3	8.0	7.7	7.4	7.1	6.8	6.5	6.3	6.1

a. Respiration

Fish use "counter-current" respiration, i.e. the in-flowing water that carries O_2 travels the opposite direction from the blood flowing through the capillaries. This maximizes the gas exchange (CO_2 unloaded, O_2 loaded) across the gills. The figure below demonstrates this principle and compares it to "co-current" flow.

With co-current flow, only 1/2 of the temp is extracted from the hot water tube

Up to 80% of the temp is extracted with counter-current flow

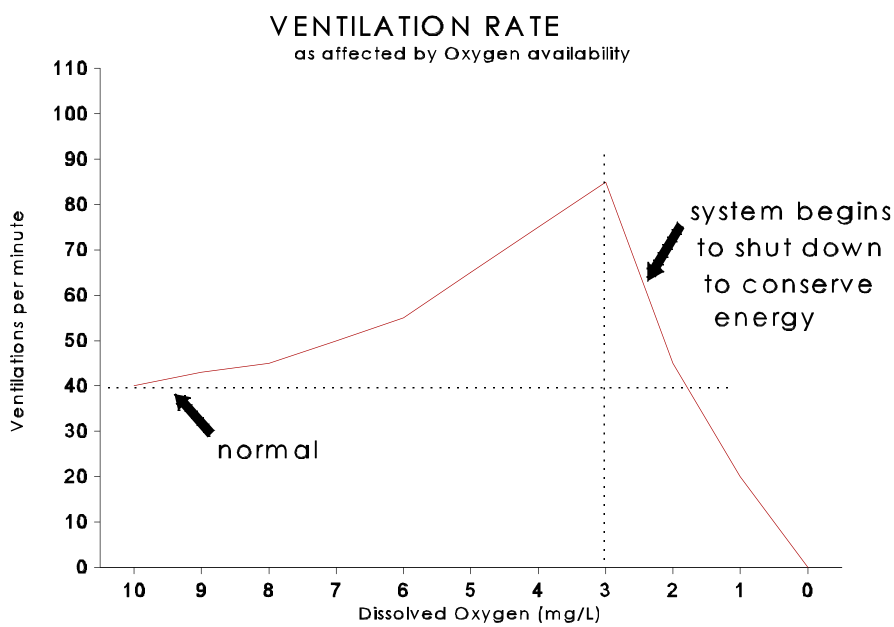


1) <u>Fish Size:</u>

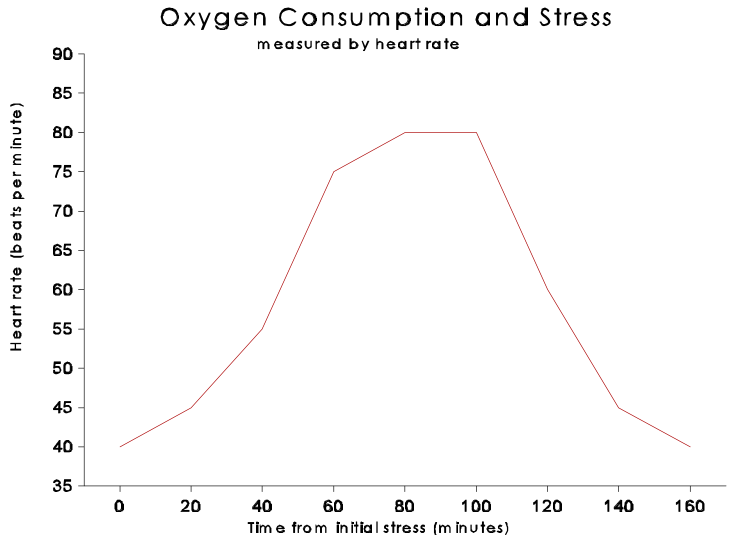
Oxygen consumption (mg/hr) at average activity levels as a function of fish size for coho salmon and rainbow trout. Note the dramatic increase in actual consumption with size (but the decrease in consumption per body weight) and the much greater oxygen needs of rainbow trout.

Fish size		O_2 consumed at 10°C mg/hr (mg/hr/kg)			
inches	grams	trout		salmon	
1	0.2	0.08	(400)	0.07	(350)
2	1.5	0.5	(333)	0.3	(200)
3	4.9	1.5	(306)	1.0	(204)
4	11.8	3.2	(271)	1.9	(161)
5	22.9	5.7	(249)	3.3	(144)
6	39.7	9.0	(227)	5.1	(129)
7	63.5	13.8	(217)	7.4	(117)
8	94.3	19.3	(205)	10.2	(108)

2) <u>Availability:</u> Oxygen requirements are also affected by its availability. As the DO drops, fish begin to respire faster in an attempt to utilize the O_2 present in the water. The chart below illustrates this.



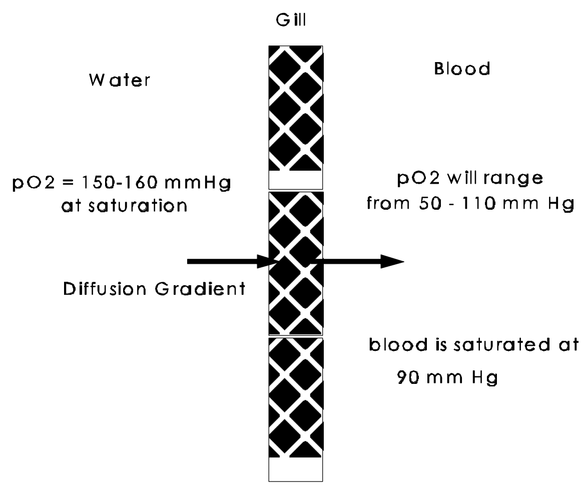
3) Stress: Oxygen requirements are further affected by "stress". Whenever a fish is stressed, adrenaline is produced, causing its heart rate to increase, thus increasing its demand for O_2. The chart below illustrates this.



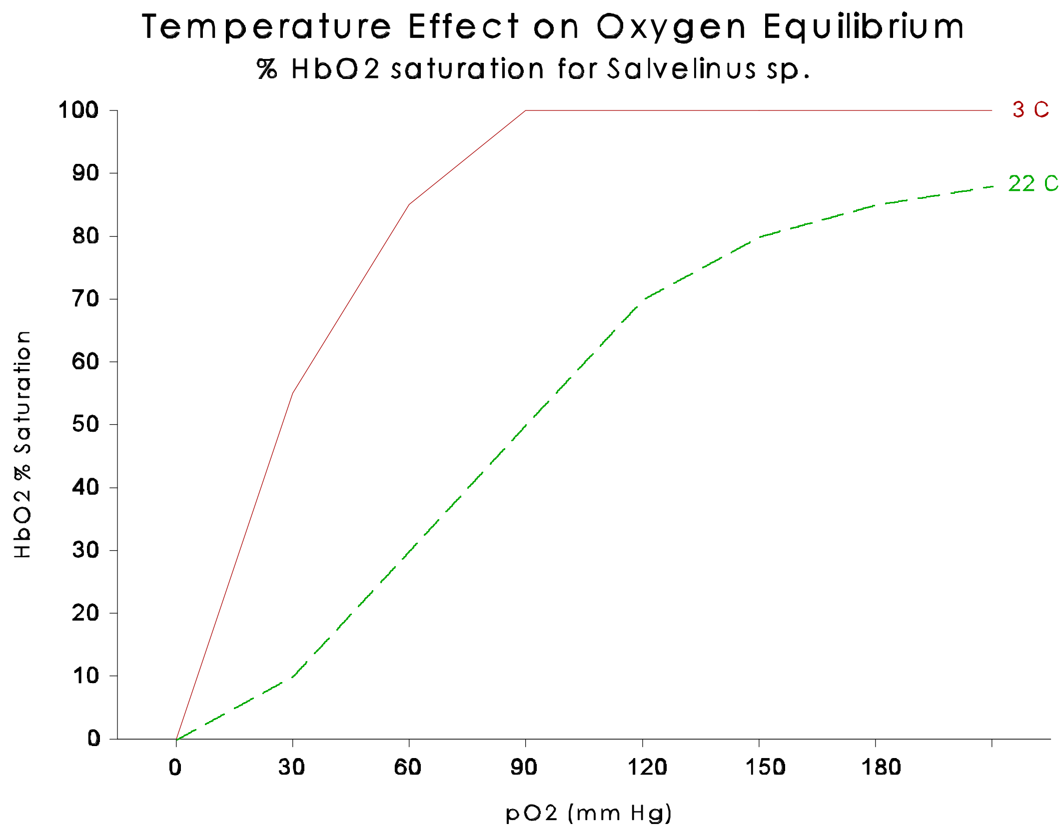
4) Partial Pressure of O_2 as well as temperature influence how well the hemoglobin (Hb) can pick up and hold O_2. The table below gives sea-level pO_2 values for corresponding DO levels. The figure shows how pO_2 level in water affects the saturation level of Hb. Below a pO_2 of 90 mm Hg, a fish cannot saturate its Hb with O_2.

at 10°C

D.O.	pO_2
12 ppm	157.2 mm Hg
8 ppm	126 mm Hg
6 ppm	94.5 mm Hg
4 ppm	62.8 mm Hg
2 ppm	31.4 mm Hg



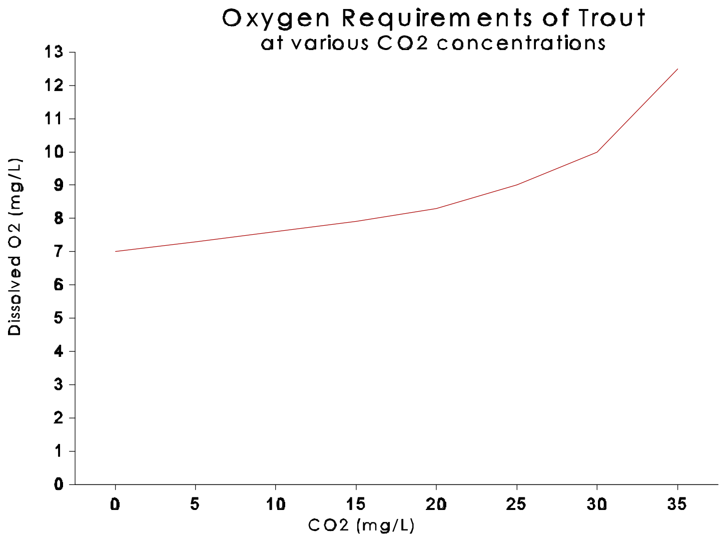
5) Temperature: Because temperature influences the solubility of a gas in a liquid, as temperature increases, solubility of oxygen in the water decreases. Corresponding to this decreased solubility, pO_2 in the water also decreases, decreasing the gas exchange efficiency across the gills. The result, when the O_2 pressure is low enough (dependent upon fish species), is an inability of the fish to saturate its Hb with O_2. The chart below illustrates this relationship.

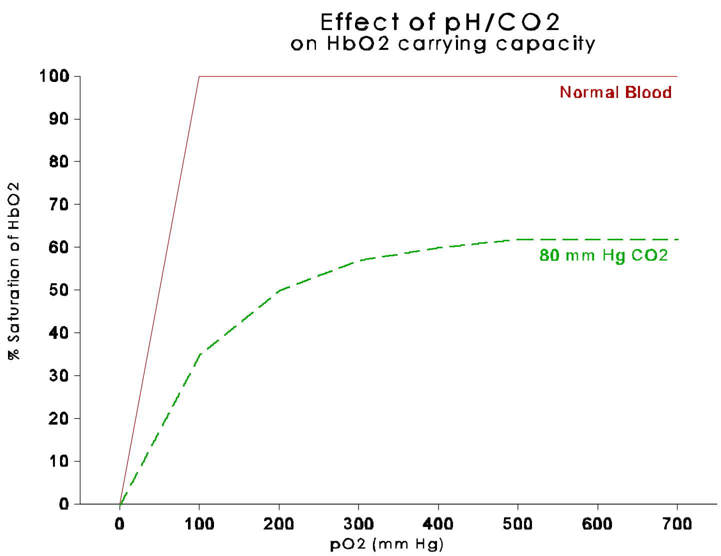


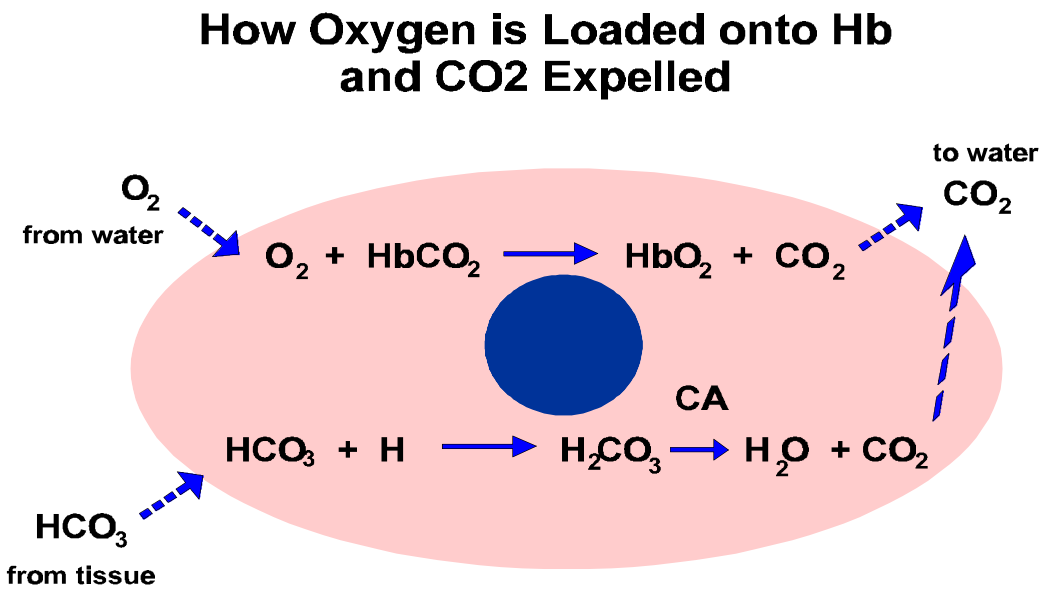
Any one of the above listed factors, or a combination of them, can contribute to increased respiration rates. When these situations are encountered by a fish, if not corrected, will produce a "snow-ball" effect, which over time only makes matters worse. As the fish's demand for O_2 increases, its respiration rate increases, which in turn increases its demand for O_2, which in turn increases its respiration rate, etc. etc..

b. Blood Chemistry

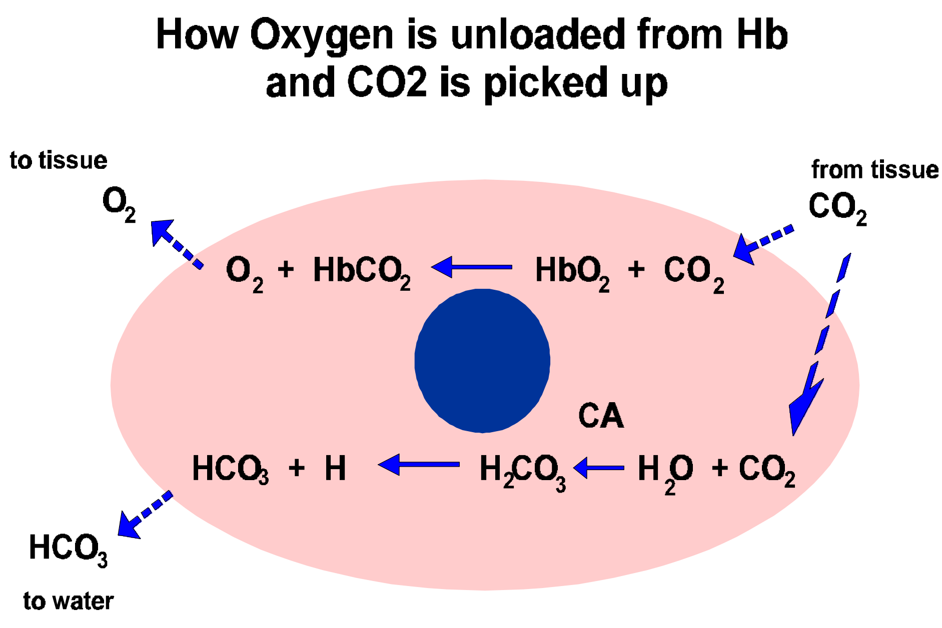
Carbon dioxide (CO_2) and pH are both factors that influence O_2 uptake from the water by a fish. For the most part, CO_2 regulates the pH of the blood- the more CO_2 in the blood, the lower the pH. When the pH drops too low, below 7.8, "acidosis" begins to occur. A decrease in pH decreases the ability of the Hb to bind O_2. Thus, as with temperature and partial pressure, fish with "acidosis" can not saturate their blood with O_2. The charts below are examples of this.







Red Blood Cell in the Gill Lamella



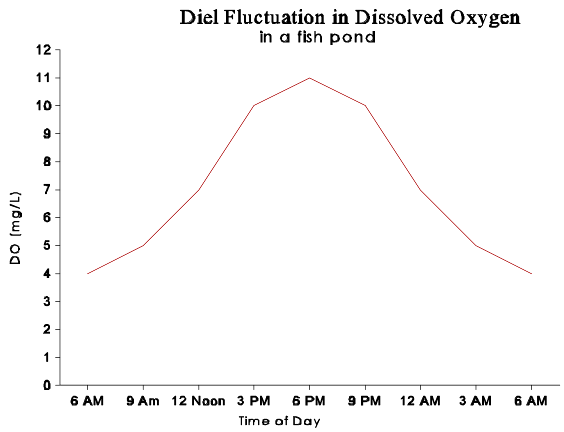
Red Blood Cell in tissue

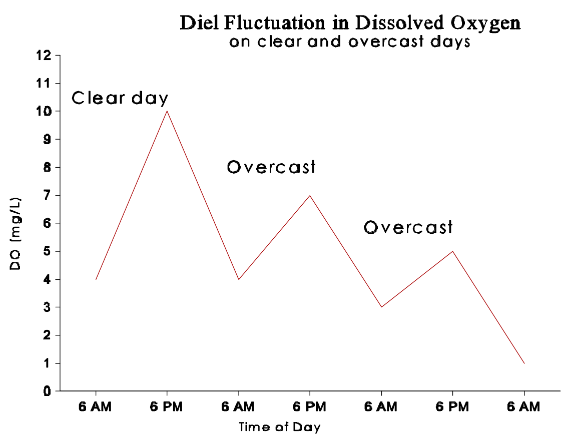
c. Sources of O_2

1) Phytoplankton and other aquatic plants are a major source of DO in slack water and reservoirs. During peak photosynthesis, they can even produce supersaturation. However, plants only produce oxygen during the sunny part of the day- at night and on overcast days, plants respire, using O_2 while producing CO_2.

2) Air-water Interface is where O_2 diffuses from the atmosphere into the water. When waters are calm, there is little gas exchange; when the surface is moving, by wind, flow,or artificially, gas exchange is promoted. (This process is very similar to that of "counter-current" flow across the gills).

The charts below are examples of how oxygen cycles through time in a pond.





2. Water Temperature

A fish's body temperature, with a few exceptions, is about 0.5ºC (1.0ºF) above that of its environment. Consequently, the body temperature of fish is governed by the water temperature and as a result, water temperature plays a very important role in regulating the activities of fish.

In any organism, life is the result of thousands of integrated rate-regulated biochemical reactions. Protien catalysts called ***enzymes*** are extremely important in the regulation of these reactions. At the relatively narrow temperature range at which life can exist, without enzymes, rates of biochemical reactions would occur much too slowly for life. Enzymes, however, lower the free activation energy of the reactants, which simply stated means that in the presence of enzymes, reactions can occur at the rates necessary for life at our low earthly temperatures. It is somewhat of a paradox that enzymes, which are so important in the relationship between temperature and regulation of biochemical reactions, are among the most sensitive of the biochemical materials to temperature change. In warm blooded animals such as man, this is normally not a problem because the body temperature generally remains constant regardless of the environmental temperature. However, if the body temperature of a warm blooded animal does change several degrees, it is a matter of concern, and if the body temperature changes much more, it can be fatal, one of the reasons being the deterioration of the enzymes and the resulting breakdown in the integrity of critical biochemical reactions.

Fish are ***cold-blooded*** animals and therefore their body temperature (and the temperature at which their enzyme systems work) is regulated by the water temperature. With this in mind, fish have evolved a biological strategy to overcome this dilemma- it has been demonstrated that fish can produce ***variants*** of enzymes such that in cold water a fish produces the variant of an enzyme that is more efficient at colder temperatures and in warm water fish produce a variant that is more efficient in warm water.

In nature, changes in water temperature generally occur gradually over weeks or months, which allow a fish time to produce the necessary enzyme variants and make whatever other physiological adjustments are necessary for it to function within a given temperature range. However, if a fish is subjected to sudden changes in water temperature, as often occurs in situations involving distribution, the fish may die before they can make the necessary physiological adjustments. ***Therefore, the best practice is to acclimate fish slowly.***

3. Carbon Dioxide (CO_2)

Carbon dioxide is a normal constituent of air (about 0.04%) and is highly water soluble. However, it occurs in water mainly as a product of organic decomposition.

<u>CO_2</u>	
0 - 5 mg/L	good
> 20 mg/L	stress
> 100 mg/L	anesthesia

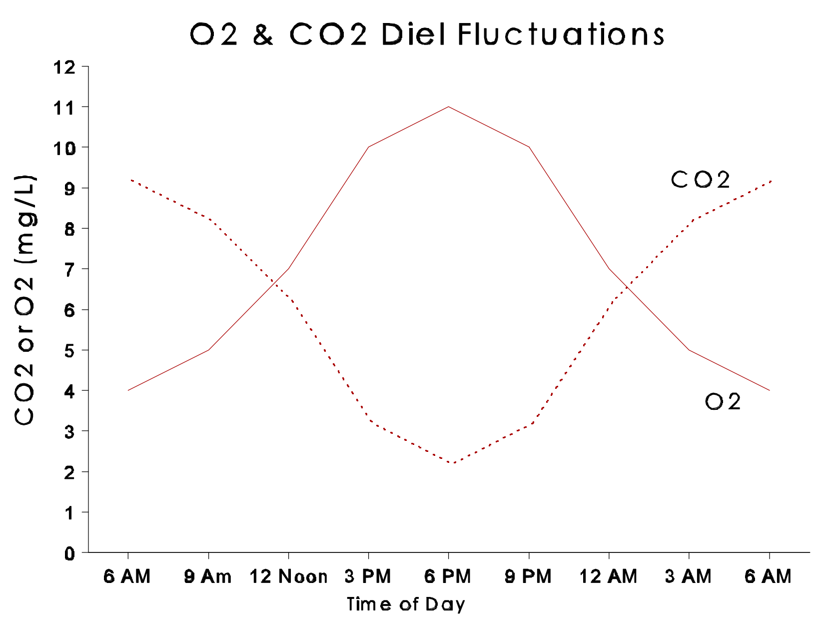
a. Solubility of CO_2

$H_2O + CO_2 \rightleftharpoons H_2CO_3$ (carbonic acid) [less than 1%]
$H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$ (bicarbonate) [very strong dissociation]
Total CO_2 ($CO_2 + H_2CO_3$) $+ H_2O \rightleftharpoons H^+ + HCO_3^-$

HCO_3^- dissociates further:

$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}$ (carbonate)
$CO_2 = CO_3^{2-}$ at pH 8.34

above pH 8.34 CO_2 is absent
below pH 8.34 CO_3^{2-} is absent



b. Relationship to Alkalinity and Hardness- pH regulation

Bicarbonate (HCO_3^-) and Carbonate (CO_3^{2-})

Natural waters usually contain more HCO_3^- than results from the ionization of H_2CO_3 in water saturated with CO_2. The CO_2 present reacts with bases in soil and rock to form HCO_3^-. Calcite ($CaCO_3$) and Dolomite ($CaMg(CO_3)_2$) are examples:

$$CaCO_3 + CO_2 + H_2O \rightleftharpoons Ca^{2+} + 2HCO_3^-$$

Reactions involving the formation of HCO_3^- from carbonates are **equilibrium** reactions- a certain amount of CO_2 must be present to maintain a given amount of HCO_3^- in solution. Therefore, if the amount of CO_2 at equilibrium is increased or decreased, there will be a corresponding change in the concentration of HCO_3^-.

$$HCO_3^- + H^+ \rightleftharpoons H_2O + CO_2 \quad \text{(base)}$$

$$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-} \qquad \text{(acid)}$$

H^+ ions produced in the second reaction are "used up" in the first reaction, therefore solutions of HCO_3^- are weakly alkaline (pH 8.34)

CO_3^{2-} is hydrolyzed to give OH^- :

$$CO_3^{2-} + H_2O \rightleftharpoons HCO_3^- + OH^-$$

CO_3^{2-} is a stronger base than CO_2 is an acid, therefore OH^- will exceed H^+ in a solution of HCO_3^- at equilibrium:

$$2HCO_3^- \rightleftharpoons CO_2 + CO_3^{2-} + H_2O$$

As CO_2 is removed from solution, CO_3^{2-} increases causing the pH to rise:

$$[H^+] = \frac{K_1K_2\ [\text{total } CO_2]}{(CO_3^{2-})}$$

H^+ is **directly** proportional to CO_2 and **indirectly** proportional to CO_3^{2-}

c. Source of CO_2

CO_2 primarily comes from organic decomposition. However, it is also produced by respiring animals and plants. In waters with heavy algal growth or large numbers of aquatic plants, nighttime production of CO_2 can be quite high.

4. Alkalinity

Alkalinity is the "ability/capacity of the water to accept protons"; "the quantity and kinds of compounds that collectively shift the pH to Alkaline". More simply put, alkalinity is the "**buffering**" capacity (resist pH change) of the water.

a. Types:

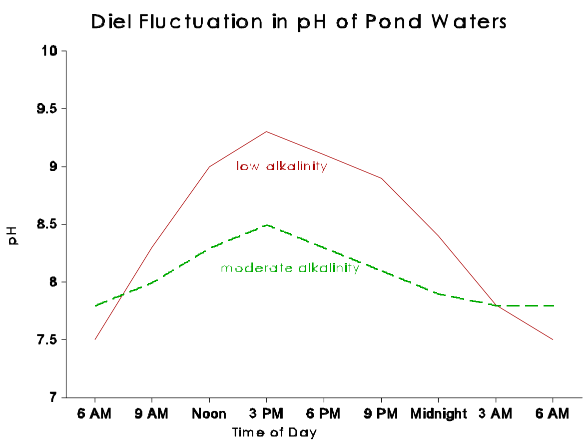
Carbonate (CO_3^{2-})
Bicarbonate (HCO_3^-)
Hydroxide (OH^-) this occurs rarely in nature

Alkalinity is measured in terms of $CaCO_3$

b. Buffering:

$H^+ \uparrow \quad H^+ + HCO_3^- \rightharpoonup CO_2 + H_2O$ (H^+ used up to keep pH up)

$OH^- \uparrow \quad CO_2 + H_2O \rightharpoonup HCO_3^- + H^+$ (H^+ liberated to keep pH down)



5. **Hardness**

Hardness is the "capacity of water to precipitate soap when shaken with sand to form lather lasting 5 minutes"; "the total concentration of Ca^{2+} and Mg^{2+} ions".

Hardness is one of the components of total dissolved solids and is primarily a function of the amounts of calcium and magnesium ions in the water. Other metals such as iron, copper, zinc, aluminum, and lead can also add to total hardness, but these are usually only found in trace amounts.

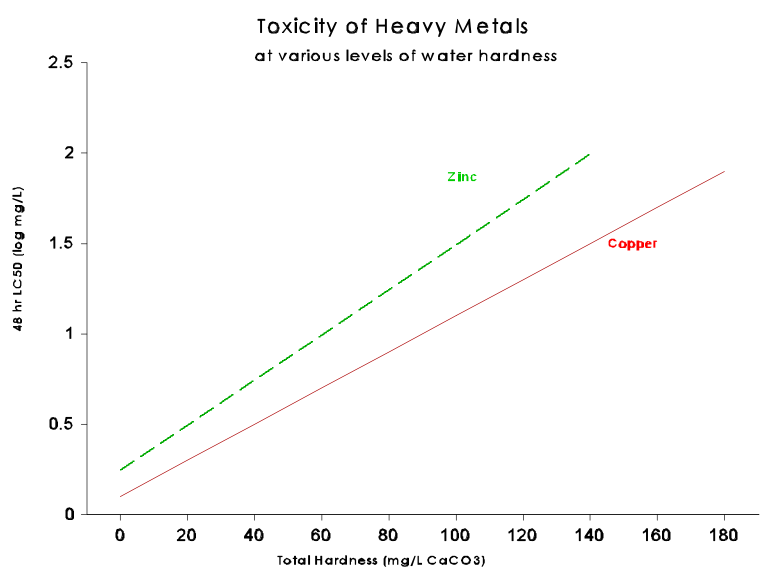
a. **Classification of waters:**

1) Very soft water-	< 10 mg/L ($CaCO_3$)
2) Soft " -	10 - 100 mg/L
3) Hard " -	100 - 200 mg/L
4) Very hard " -	> 200 mg/L

Soft waters are usually acidic while hard waters are usually alkaline. Hard waters are usually more beneficial to fish because of the reduced osmotic work required to replace blood electrolytes lost via the copious urine produced by fresh water fish.

b. **Relationship to Heavy Metals**

Hard water helps to "tie-up" most heavy metals, such as copper and zinc, rendering them non-toxic to the fish. Most heavy metals will precipitate out of solution in the presence of Ca^{2+} and Mg^{2+} salts. The chart below illustrates this.



6. Ammonia (NH_3)

Ammonia occurs naturally in ground and surface waters, primarily as the result of microbial decomposition of nitrogenous organic material in the soil. Industrial discharges as well as agricultural run-off also may add ammonia.

In water, NH_3 reacts to form NH_4OH which readily dissociates to NH_4^+ and OH^- ions. The change from NH_3 to NH_4^+ is temperature and pH dependent, the amount of NH_3, being less at lower pH and temperature values.

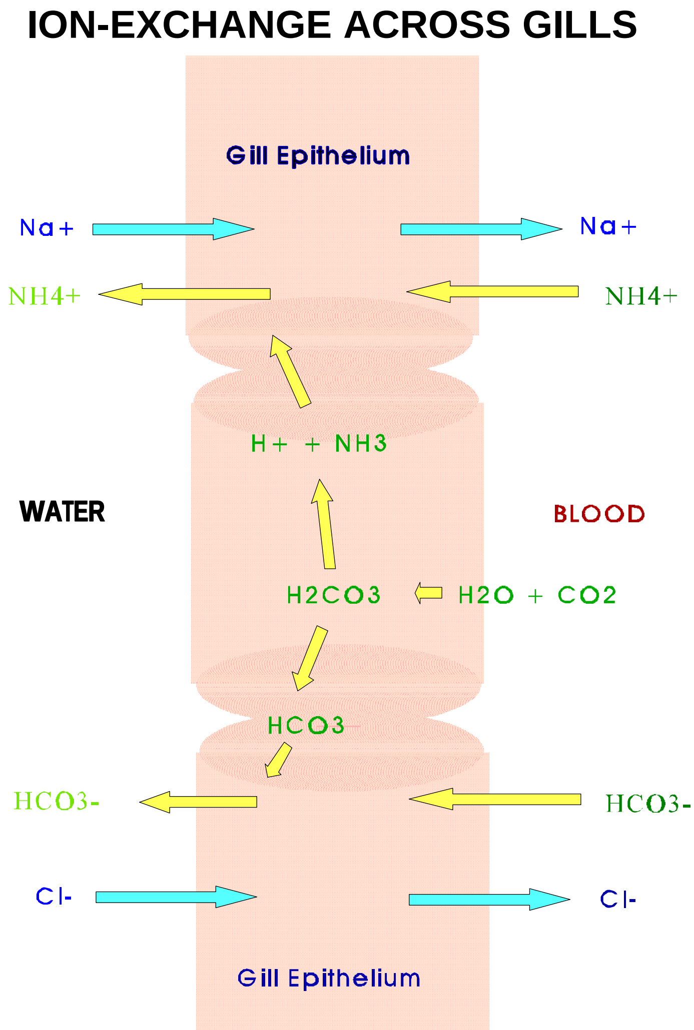
$$NH_3 + H_2O \rightleftharpoons NH_4OH \rightleftharpoons NH_4^+ + OH^-$$

The "ammonium" ion (NH_4^+) is relatively harmless to fish. However, the un-ionized molecule "ammonia" (NH_3) is quite toxic, especially to salmonids. The following table gives the percent of the un-ionized portion of total ammonia (NH_3-N) at various temperatures and pH's.

Percent of total dissolved ammonia which is unionized (toxic) as a function of pH and water temperature (from Trussel, 1972)

pH	Water Temperature (°F)				
	41	50	59	68	77
6.5	0.04	0.06	0.09	0.13	0.18
6.7	0.06	0.09	0.14	0.20	0.28
7.0	0.12	0.19	0.27	0.40	0.55
7.3	0.25	0.37	0.54	0.79	1.10
7.5	0.39	0.59	0.85	1.25	1.73
7.7	0.62	0.92	1.35	1.96	2.72
8.0	1.22	1.82	2.65	3.83	5.28
8.3	2.41	3.58	5.16	7.36	10.00
8.5	3.77	5.55	7.98	11.18	14.97
9.0	11.02	15.68	21.42	28.47	35.76

NH_4^+ is primarily excreted from the gills. Sodium ions (Na^+) are directly exchanged for NH_4^+ across the gills. NH_3 is unionized and therefore is not regulated by ion-exchange- a fish cannot recognize this compound. The diagram below shows this "ion-exchange" process.



NH_3 is toxic in very small concentration for most species of fish: usually no more than 0.0125 mg/L can be tolerated before a tissue response is seen. The most common response of a fish to NH_3 toxicity is gill lamella hyperplasia and aneurysms in gill capillaries which result in respiratory disfunction. Kidney tubules can also be damaged, resulting in osmoregulation problems.

7. Nitrite (NO_2^-)

Nitrite is an intermediate by-product of NH_3 metabolism by common soil bacteria, *Nitrosomonas sp.*. The process, known as "Nitrification", involves two species of bacteria which oxidize NH_3 to NO_2^- to NO_3^{2-} (nitrate- produced by *Nitrobacter sp*.). NO_3^{2-} is relatively harmless directly to fish. NO_2^-, however, is toxic at relatively low concentration. Most culturists agree that 0.02 mg/L NO_2^- is the maximum level for exposure. Some have reported as much as 0.2 mg/L as safe.

Nitrite toxicity is most frequently manifested by a condition called "Brown Blood Disease" or "methemoglogenemia". NO_2^- is a strong oxidizer just as oxygen is and therefore can replace the O_2 molecule in the blood. The blood is brown because the ferric (Fe^{3+}) ion is oxidized to ferrous (Fe^{2+}) ion. This condition is easily reversed by adding common salt (NaCl) to the water at a rate of 0.5 - 1% by weight of water. The Cl^- ion is readily exchanged for NO_2^- across the gills, thus allowing the oxygen to bind to the blood.

Testing and Monitoring

Parameter	Frequency	Location
Temperature	continuous	intake, outfall
pH	3 x daily	intake, outfall
Dissolved Oxygen	3 x daily	intake (outfall for reuse or last use)
N_2 (delta P from gasometer)	daily	intake
NH_4-N	daily	outfall (intake for series in reuse)
Hardness/Alkalinity	quarterly	intake
CO_2	weekly	intake, outfall
Water Flow rate	weekly or upon change	intake